

Octakis(3-methylanilinium) hexachloridocadmate tetrachloride

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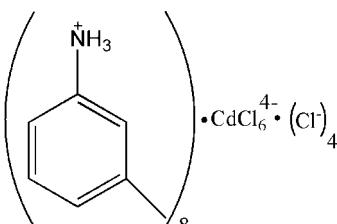
Received 17 November 2011; accepted 19 November 2011

Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.009$ Å; R factor = 0.053; wR factor = 0.144; data-to-parameter ratio = 16.6.

The asymmetric unit of the title compound, $(\text{C}_7\text{H}_{10}\text{N})_8[\text{CdCl}_6]\text{Cl}_4$, contains four 3-methylanilinium cations, two chloride anions and half an octahedral hexachloridocadmate(II) anion, which lies on an inversion centre. In the crystal, numerous $\text{N}-\text{H}\cdots\text{Cl}$ and bifurcated $\text{N}-\text{H}\cdots(\text{Cl},\text{Cl})$ hydrogen bonds link the components.

Related literature

For background to ferroelectric metal-organic complexes, see: Ye *et al.* (2009); Zhang *et al.* (2009, 2010). For a related structure, see: Liu (2011).



Experimental

Crystal data

$(\text{C}_7\text{H}_{10}\text{N})_8[\text{CdCl}_6]\text{Cl}_4$
 $M_r = 1332.18$
Triclinic, $P\bar{1}$
 $a = 8.8863$ (18) Å
 $b = 14.116$ (3) Å
 $c = 14.251$ (3) Å
 $\alpha = 87.92$ (3)°
 $\beta = 71.88$ (3)°

$\gamma = 75.20$ (3)°
 $V = 1640.8$ (6) Å³
 $Z = 1$
Mo $K\alpha$ radiation
 $\mu = 0.78$ mm⁻¹
 $T = 293$ K
0.20 × 0.20 × 0.20 mm

Data collection

Rigaku SCXmini CCD diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
 $T_{\min} = 0.860$, $T_{\max} = 0.860$

14045 measured reflections
5776 independent reflections
4134 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.064$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.053$
 $wR(F^2) = 0.144$
 $S = 0.91$
5776 reflections
348 parameters

18 restraints
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.54$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.39$ e Å⁻³

Table 1
Selected bond lengths (Å).

| | | | |
|---------|-------------|---------|-------------|
| Cd1—Cl1 | 2.5425 (12) | Cd1—Cl3 | 2.6760 (15) |
| Cd1—Cl2 | 2.6743 (13) | | |

Table 2
Hydrogen-bond geometry (Å, °).

| $D-\text{H}\cdots A$ | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|-----------------------------|--------------|--------------------|-------------|----------------------|
| N1—H1A···Cl5 ⁱ | 0.89 | 2.38 | 3.264 (5) | 176 |
| N1—H1B···Cl4 ⁱⁱ | 0.89 | 2.47 | 3.309 (5) | 157 |
| N1—H1C···Cl2 ⁱⁱⁱ | 0.89 | 2.54 | 3.329 (5) | 148 |
| N1—H1C···Cl3 ^{iv} | 0.89 | 2.88 | 3.427 (5) | 121 |
| N2—H2A···Cl4 ^v | 0.89 | 2.38 | 3.265 (5) | 176 |
| N2—H2B···Cl3 ^v | 0.89 | 2.51 | 3.300 (5) | 149 |
| N2—H2B···Cl2 ^{vi} | 0.89 | 2.93 | 3.495 (5) | 123 |
| N2—H2C···Cl5 ^{vii} | 0.89 | 2.33 | 3.186 (5) | 162 |
| N3—H3A···Cl4 | 0.89 | 2.37 | 3.254 (5) | 172 |
| N3—H3B···Cl3 ^{vii} | 0.89 | 2.61 | 3.344 (5) | 140 |
| N3—H3B···Cl2 ^{vii} | 0.89 | 2.75 | 3.367 (5) | 127 |
| N3—H3C···Cl5 ^{vi} | 0.89 | 2.44 | 3.289 (5) | 159 |
| N4—H4A···Cl4 | 0.89 | 2.40 | 3.270 (5) | 167 |
| N4—H4B···Cl5 ^{vi} | 0.89 | 2.38 | 3.267 (5) | 177 |
| N4—H4C···Cl2 | 0.89 | 2.55 | 3.305 (5) | 143 |
| N4—H4C···Cl3 | 0.89 | 2.91 | 3.526 (5) | 128 |

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x + 2, -y, -z + 1$; (iii) $x, y, z + 1$; (iv) $-x + 1, -y, -z + 1$; (v) $x, y + 1, z$; (vi) $-x + 1, -y + 1, -z$; (vii) $x + 1, y, z$.

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

The author thanks an anonymous advisor from the Ordered Matter Science Research Centre, Southeast University, for great help with the revision of this paper.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB6519).

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Zhang, W., Chen, L. Z., Xiong, R. G., Nakamura, T. & Huang, S. P. (2009). *J. Am. Chem. Soc.* **131**, 12544–12545.
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supplementary materials

Acta Cryst. (2011). **E67**, m1827 [doi:10.1107/S1600536811049464]

Octakis(3-methylanilinium) hexachloridocadmiate tetrachloride

M.-L. Liu

Comment

Recently much attention has been devoted to simple molecular-ionic compounds containing inorganic and organic ions due to the tunability of their special structural features and their potential ferroelectrics property. Ferroelectric materials that exhibit reversible electric polarization in response to an external electric field have found many applications such as nonvolatile memory storage, electronics and optics. The freezing of a certain functional group at low temperature forces significant orientational motions of the guest molecules and thus induces the formation of the ferroelectric phase. (Zhang *et al.* 2009; Ye *et al.* 2009; Zhang *et al.* 2010.). In our laboratory, the title compound, (I), has been synthesized and its crystal structure is herein reported.

The title compound, $[(C_7H_{10}N)_8CdCl_6]Cl_4$, has an asymmetric unit that consists of four 3-methylanilinium cations, two chloride anions and one hexachloridocadmiumate anion (Fig 1), which lies in a symmetrical center. The non-hydrogen atoms of $C_7H_{10}N$ cations are nearly coplanar, the cadmium atom is coordinated by six chloride ions, forming a distorted octahedron, the average Cd—Cl bond distances range from 2.5425 (12) Å to 2.6760 (15) Å, the Cl—Cd—Cl angles range from 88.87 (5)° to 180°. The existence of N—H···Cl hydrogen-bonding interactions makes great contribution to the stability of the crystal structure (Fig 2).

Experimental

3.21 g (0.03 mol) of 3-methylbenzylamine was firstly dissolved in 30 ml ethanol, to which 1.1 g (0.03 mol) of hydrochloric acid was then added to afford the solution, then the 0.83 g (0.01 mol) cadmium chloride was dissolved in 20 ml ethanol which was added hydrochloric acid, at last, mixed the above solution without any precipitation under stirring at the ambient temperature. Single crystals suitable for X-ray structure analysis were obtained by the slow evaporation of the above solution after 4 days in air.

The dielectric constant of the compound as a function of temperature indicates that the permittivity is basically temperature-independent ($\epsilon = C/(T-T_0)$), suggesting that this compound is not ferroelectric or there may be no distinct phase transition occurring within the measured temperature within the measured temperature (below the melting point).

Refinement

H atoms were placed in calculated positions (N—H = 0.89 Å; C—H = 0.93 Å for Csp^2 atoms and C—H = 0.96 Å and 0.97 Å for Csp^3 atoms), assigned fixed U_{iso} values [$U_{iso} = 1.2U_{eq}(Csp^2)$ and $1.5U_{eq}(Csp^3, N)$] and allowed to ride.

supplementary materials

Figures

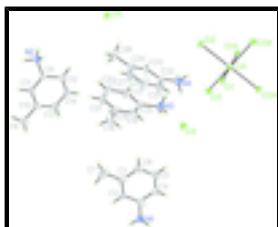


Fig. 1. The molecular structure of the title compound, showing 30% probability displacement ellipsoids.

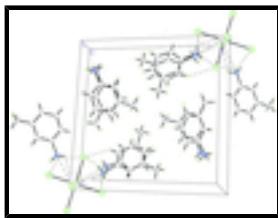


Fig. 2. Crystal structure of the title compound with view along the a axis. Intermolecular interactions are shown as dashed lines.

Octakis(3-methylanilinium) hexachloridocadmate tetrachloride

Crystal data

| | |
|-------------------------------|---|
| $(C_7H_{10}N)_8[CdCl_6]Cl_4$ | $V = 1640.8 (6) \text{ \AA}^3$ |
| $M_r = 1332.18$ | $Z = 1$ |
| Triclinic, $P\bar{1}$ | $F(000) = 690$ |
| Hall symbol: -P 1 | $D_x = 1.348 \text{ Mg m}^{-3}$ |
| $a = 8.8863 (18) \text{ \AA}$ | Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$ |
| $b = 14.116 (3) \text{ \AA}$ | $\theta = 3.4\text{--}25^\circ$ |
| $c = 14.251 (3) \text{ \AA}$ | $\mu = 0.78 \text{ mm}^{-1}$ |
| $\alpha = 87.92 (3)^\circ$ | $T = 293 \text{ K}$ |
| $\beta = 71.88 (3)^\circ$ | Block, colourless |
| $\gamma = 75.20 (3)^\circ$ | $0.20 \times 0.20 \times 0.20 \text{ mm}$ |

Data collection

| | |
|---|---|
| Rigaku SCXmini CCD diffractometer | 5776 independent reflections |
| Radiation source: fine-focus sealed tube graphite | 4134 reflections with $I > 2\sigma(I)$ |
| CCD_Profile_fitting scans | $R_{\text{int}} = 0.064$ |
| Absorption correction: multi-scan (<i>CrystalClear</i> ; Rigaku, 2005) | $\theta_{\text{max}} = 25.0^\circ, \theta_{\text{min}} = 3.0^\circ$ |
| $T_{\text{min}} = 0.860, T_{\text{max}} = 0.860$ | $h = -10 \rightarrow 10$ |
| 14045 measured reflections | $k = -16 \rightarrow 16$ |
| | $l = -16 \rightarrow 16$ |

Refinement

| | |
|----------------------------|--|
| Refinement on F^2 | Primary atom site location: structure-invariant direct methods |
| Least-squares matrix: full | Secondary atom site location: difference Fourier map |

| | |
|---------------------------------|---|
| $R[F^2 > 2\sigma(F^2)] = 0.053$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.144$ | H-atom parameters constrained |
| $S = 0.91$ | $w = 1/[\sigma^2(F_o^2) + (0.0846P)^2 + 0.9416P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| 5776 reflections | $(\Delta/\sigma)_{\text{max}} = 0.074$ |
| 348 parameters | $\Delta\rho_{\text{max}} = 0.54 \text{ e \AA}^{-3}$ |
| 18 restraints | $\Delta\rho_{\text{min}} = -0.39 \text{ e \AA}^{-3}$ |

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2 , conventional R-factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F , and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|-------------|------------|------------|----------------------------------|
| N1 | 0.8397 (6) | 0.1086 (3) | 0.7966 (3) | 0.0507 (11) |
| H1A | 0.8672 | 0.1473 | 0.8329 | 0.076* |
| H1B | 0.9020 | 0.0477 | 0.7935 | 0.076* |
| H1C | 0.7349 | 0.1089 | 0.8241 | 0.076* |
| C1 | 0.8646 (6) | 0.1450 (4) | 0.6958 (4) | 0.0443 (13) |
| C2 | 0.9124 (6) | 0.2302 (4) | 0.6733 (4) | 0.0483 (13) |
| H2 | 0.9252 | 0.2660 | 0.7225 | 0.058* |
| C3 | 0.9416 (7) | 0.2637 (4) | 0.5790 (4) | 0.0578 (16) |
| C4 | 0.8444 (7) | 0.0901 (4) | 0.6257 (4) | 0.0592 (15) |
| H4 | 0.8137 | 0.0318 | 0.6416 | 0.071* |
| C5 | 0.8702 (8) | 0.1226 (5) | 0.5312 (5) | 0.0686 (18) |
| H5 | 0.8537 | 0.0874 | 0.4830 | 0.082* |
| C6 | 0.9207 (8) | 0.2074 (5) | 0.5084 (4) | 0.0665 (18) |
| H6 | 0.9414 | 0.2276 | 0.4439 | 0.080* |
| C7 | 0.9997 (10) | 0.3560 (5) | 0.5545 (5) | 0.087 (2) |
| H7A | 1.0879 | 0.3451 | 0.4933 | 0.130* |
| H7B | 1.0374 | 0.3729 | 0.6063 | 0.130* |
| H7C | 0.9109 | 0.4086 | 0.5483 | 0.130* |
| C8 | 0.6267 (8) | 0.8805 (5) | 0.5669 (4) | 0.0725 (19) |
| H8A | 0.5254 | 0.8858 | 0.6189 | 0.109* |
| H8B | 0.6492 | 0.9438 | 0.5575 | 0.109* |
| H8C | 0.7139 | 0.8355 | 0.5842 | 0.109* |
| N2 | 0.7149 (5) | 0.9027 (3) | 0.2064 (3) | 0.0496 (11) |
| H2A | 0.7556 | 0.9510 | 0.2179 | 0.074* |

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|------|-------------|------------|------------|--------------|
| H2B | 0.6314 | 0.9273 | 0.1834 | 0.074* |
| H2C | 0.7925 | 0.8593 | 0.1620 | 0.074* |
| C9 | 0.6575 (6) | 0.8539 (4) | 0.2994 (4) | 0.0389 (12) |
| C10 | 0.6136 (7) | 0.8436 (4) | 0.4724 (4) | 0.0495 (14) |
| C11 | 0.6709 (6) | 0.8869 (4) | 0.3835 (4) | 0.0421 (12) |
| H11 | 0.7186 | 0.9387 | 0.3820 | 0.050* |
| C12 | 0.5901 (7) | 0.7776 (4) | 0.2968 (4) | 0.0546 (15) |
| H12 | 0.5832 | 0.7556 | 0.2380 | 0.065* |
| C13 | 0.5448 (7) | 0.7675 (5) | 0.4711 (4) | 0.0608 (16) |
| H13 | 0.5058 | 0.7375 | 0.5297 | 0.073* |
| C14 | 0.5323 (8) | 0.7343 (5) | 0.3850 (5) | 0.0681 (18) |
| H14 | 0.4848 | 0.6826 | 0.3859 | 0.082* |
| C16 | 0.7077 (9) | 0.4512 (5) | 0.3820 (5) | 0.094 (2) |
| H16A | 0.7335 | 0.4948 | 0.4213 | 0.140* |
| H16B | 0.6992 | 0.3919 | 0.4159 | 0.140* |
| H16C | 0.6054 | 0.4822 | 0.3711 | 0.140* |
| C15 | 1.0231 (6) | 0.3114 (4) | 0.1562 (4) | 0.0459 (13) |
| N3 | 1.0857 (5) | 0.2101 (3) | 0.1154 (3) | 0.0500 (11) |
| H3A | 1.0286 | 0.1724 | 0.1545 | 0.075* |
| H3B | 1.1908 | 0.1885 | 0.1115 | 0.075* |
| H3C | 1.0758 | 0.2079 | 0.0553 | 0.075* |
| C17 | 1.0827 (8) | 0.3832 (5) | 0.1010 (5) | 0.0707 (18) |
| H17 | 1.1632 | 0.3677 | 0.0399 | 0.085* |
| C18 | 0.9049 (7) | 0.3321 (4) | 0.2458 (4) | 0.0504 (14) |
| H18 | 0.8673 | 0.2816 | 0.2812 | 0.061* |
| C19 | 0.8402 (7) | 0.4276 (4) | 0.2847 (5) | 0.0587 (16) |
| C20 | 1.0205 (10) | 0.4790 (5) | 0.1385 (6) | 0.086 (2) |
| H20 | 1.0587 | 0.5290 | 0.1026 | 0.103* |
| C21 | 0.9007 (9) | 0.5002 (5) | 0.2298 (6) | 0.075 (2) |
| H21 | 0.8601 | 0.5649 | 0.2548 | 0.090* |
| N4 | 0.6578 (6) | 0.2081 (3) | 0.1049 (4) | 0.0551 (12) |
| H4A | 0.6956 | 0.1702 | 0.1481 | 0.083* |
| H4B | 0.7416 | 0.2172 | 0.0548 | 0.083* |
| H4C | 0.5971 | 0.1793 | 0.0821 | 0.083* |
| C22 | 0.5575 (7) | 0.3031 (4) | 0.1537 (4) | 0.0458 (13) |
| C23 | 0.5977 (7) | 0.3871 (4) | 0.1165 (4) | 0.0511 (14) |
| H23 | 0.6900 | 0.3836 | 0.0620 | 0.061* |
| C24 | 0.5009 (8) | 0.4776 (4) | 0.1602 (5) | 0.0579 (15) |
| C25 | 0.4232 (10) | 0.3057 (5) | 0.2339 (5) | 0.088 (2) |
| H25 | 0.3969 | 0.2481 | 0.2584 | 0.105* |
| C26 | 0.3282 (11) | 0.3950 (6) | 0.2776 (6) | 0.112 (2) |
| H26 | 0.2360 | 0.3982 | 0.3321 | 0.134* |
| C27 | 0.3685 (10) | 0.4804 (5) | 0.2410 (5) | 0.088 (2) |
| H27 | 0.3042 | 0.5406 | 0.2720 | 0.105* |
| C28 | 0.5396 (11) | 0.5721 (5) | 0.1201 (6) | 0.098 (3) |
| H28A | 0.4503 | 0.6266 | 0.1526 | 0.147* |
| H28B | 0.5553 | 0.5720 | 0.0503 | 0.147* |
| H28C | 0.6377 | 0.5777 | 0.1319 | 0.147* |
| Cd1 | 0.5000 | 0.0000 | 0.0000 | 0.03328 (17) |

| | | | | |
|-----|--------------|--------------|--------------|------------|
| Cl1 | 0.78766 (14) | -0.00243 (8) | -0.00119 (8) | 0.0353 (3) |
| Cl2 | 0.45880 (15) | 0.18683 (8) | -0.05106 (9) | 0.0418 (3) |
| Cl3 | 0.38016 (15) | 0.06130 (9) | 0.19060 (9) | 0.0436 (3) |
| Cl4 | 0.84395 (16) | 0.08670 (9) | 0.25439 (10) | 0.0476 (3) |
| Cl5 | 0.04194 (17) | 0.75072 (10) | 0.07936 (10) | 0.0501 (3) |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|------------|------------|------------|-------------|-------------|-------------|
| N1 | 0.053 (3) | 0.055 (3) | 0.044 (3) | -0.020 (2) | -0.012 (2) | 0.013 (2) |
| C1 | 0.036 (3) | 0.055 (3) | 0.035 (3) | -0.005 (2) | -0.006 (2) | 0.008 (2) |
| C2 | 0.053 (3) | 0.048 (3) | 0.041 (3) | -0.011 (3) | -0.012 (3) | 0.006 (3) |
| C3 | 0.048 (3) | 0.058 (4) | 0.050 (4) | -0.003 (3) | -0.002 (3) | 0.017 (3) |
| C4 | 0.070 (4) | 0.050 (4) | 0.057 (4) | -0.013 (3) | -0.020 (3) | 0.003 (3) |
| C5 | 0.078 (5) | 0.077 (5) | 0.046 (4) | -0.007 (4) | -0.023 (3) | -0.007 (3) |
| C6 | 0.069 (4) | 0.073 (5) | 0.039 (3) | 0.005 (3) | -0.010 (3) | 0.007 (3) |
| C7 | 0.093 (5) | 0.079 (5) | 0.078 (5) | -0.032 (4) | -0.007 (4) | 0.034 (4) |
| C8 | 0.081 (5) | 0.086 (5) | 0.043 (4) | -0.011 (4) | -0.017 (3) | 0.000 (3) |
| N2 | 0.051 (3) | 0.062 (3) | 0.035 (2) | -0.015 (2) | -0.014 (2) | 0.012 (2) |
| C9 | 0.037 (3) | 0.040 (3) | 0.034 (3) | -0.005 (2) | -0.008 (2) | 0.008 (2) |
| C10 | 0.049 (3) | 0.059 (4) | 0.035 (3) | -0.006 (3) | -0.013 (3) | 0.005 (3) |
| C11 | 0.046 (3) | 0.044 (3) | 0.035 (3) | -0.011 (2) | -0.012 (2) | 0.004 (2) |
| C12 | 0.069 (4) | 0.044 (3) | 0.056 (4) | -0.011 (3) | -0.031 (3) | 0.005 (3) |
| C13 | 0.063 (4) | 0.070 (4) | 0.048 (4) | -0.024 (3) | -0.013 (3) | 0.023 (3) |
| C14 | 0.082 (5) | 0.050 (4) | 0.082 (5) | -0.029 (3) | -0.031 (4) | 0.015 (3) |
| C16 | 0.101 (6) | 0.077 (5) | 0.075 (5) | 0.010 (4) | -0.010 (4) | -0.032 (4) |
| C15 | 0.050 (3) | 0.033 (3) | 0.051 (3) | -0.007 (2) | -0.014 (3) | -0.003 (2) |
| N3 | 0.049 (3) | 0.038 (3) | 0.057 (3) | -0.006 (2) | -0.012 (2) | -0.010 (2) |
| C17 | 0.079 (5) | 0.052 (4) | 0.072 (4) | -0.023 (3) | -0.006 (4) | 0.003 (3) |
| C18 | 0.056 (3) | 0.040 (3) | 0.053 (3) | -0.007 (3) | -0.018 (3) | -0.002 (3) |
| C19 | 0.063 (4) | 0.046 (4) | 0.060 (4) | 0.004 (3) | -0.022 (3) | -0.013 (3) |
| C20 | 0.113 (6) | 0.045 (4) | 0.101 (6) | -0.035 (4) | -0.026 (5) | 0.021 (4) |
| C21 | 0.092 (5) | 0.035 (4) | 0.092 (5) | -0.004 (3) | -0.027 (4) | -0.015 (3) |
| N4 | 0.065 (3) | 0.034 (3) | 0.069 (3) | -0.009 (2) | -0.027 (3) | -0.005 (2) |
| C22 | 0.055 (3) | 0.035 (3) | 0.051 (3) | -0.006 (2) | -0.026 (3) | 0.003 (2) |
| C23 | 0.052 (3) | 0.041 (3) | 0.052 (3) | -0.011 (3) | -0.005 (3) | 0.002 (3) |
| C24 | 0.067 (4) | 0.040 (3) | 0.065 (4) | -0.012 (3) | -0.019 (3) | 0.009 (3) |
| C25 | 0.115 (5) | 0.048 (4) | 0.069 (4) | -0.027 (4) | 0.021 (4) | 0.000 (3) |
| C26 | 0.117 (5) | 0.075 (4) | 0.095 (4) | -0.020 (4) | 0.030 (4) | -0.006 (4) |
| C27 | 0.097 (5) | 0.046 (4) | 0.087 (5) | -0.006 (4) | 0.010 (4) | -0.019 (3) |
| C28 | 0.119 (7) | 0.051 (4) | 0.121 (7) | -0.036 (4) | -0.023 (6) | 0.019 (4) |
| Cd1 | 0.0356 (3) | 0.0329 (3) | 0.0336 (3) | -0.0111 (2) | -0.0123 (2) | 0.0032 (2) |
| Cl1 | 0.0363 (6) | 0.0349 (6) | 0.0361 (6) | -0.0119 (5) | -0.0111 (5) | 0.0029 (5) |
| Cl2 | 0.0473 (7) | 0.0325 (7) | 0.0476 (7) | -0.0118 (5) | -0.0174 (6) | 0.0086 (5) |
| Cl3 | 0.0475 (7) | 0.0479 (8) | 0.0341 (7) | -0.0119 (6) | -0.0109 (6) | -0.0017 (5) |
| Cl4 | 0.0552 (8) | 0.0414 (7) | 0.0449 (7) | -0.0151 (6) | -0.0123 (6) | 0.0069 (6) |
| Cl5 | 0.0612 (9) | 0.0426 (8) | 0.0430 (7) | -0.0103 (6) | -0.0136 (6) | -0.0006 (6) |

supplementary materials

Geometric parameters (\AA , $^\circ$)

| | | | |
|------------|-----------|----------------------|-------------|
| N1—C1 | 1.478 (6) | C16—H16C | 0.9600 |
| N1—H1A | 0.8900 | C15—C18 | 1.362 (7) |
| N1—H1B | 0.8900 | C15—C17 | 1.372 (8) |
| N1—H1C | 0.8900 | C15—N3 | 1.464 (6) |
| C1—C4 | 1.367 (8) | N3—H3A | 0.8900 |
| C1—C2 | 1.371 (7) | N3—H3B | 0.8900 |
| C2—C3 | 1.377 (7) | N3—H3C | 0.8900 |
| C2—H2 | 0.9300 | C17—C20 | 1.380 (9) |
| C3—C6 | 1.387 (9) | C17—H17 | 0.9300 |
| C3—C7 | 1.512 (9) | C18—C19 | 1.383 (7) |
| C4—C5 | 1.375 (8) | C18—H18 | 0.9300 |
| C4—H4 | 0.9300 | C19—C21 | 1.384 (9) |
| C5—C6 | 1.377 (9) | C20—C21 | 1.385 (10) |
| C5—H5 | 0.9300 | C20—H20 | 0.9300 |
| C6—H6 | 0.9300 | C21—H21 | 0.9300 |
| C7—H7A | 0.9600 | N4—C22 | 1.465 (7) |
| C7—H7B | 0.9600 | N4—H4A | 0.8900 |
| C7—H7C | 0.9600 | N4—H4B | 0.8900 |
| C8—C10 | 1.509 (8) | N4—H4C | 0.8900 |
| C8—H8A | 0.9600 | C22—C25 | 1.365 (8) |
| C8—H8B | 0.9600 | C22—C23 | 1.366 (7) |
| C8—H8C | 0.9600 | C23—C24 | 1.386 (8) |
| N2—C9 | 1.478 (6) | C23—H23 | 0.9300 |
| N2—H2A | 0.8900 | C24—C27 | 1.359 (9) |
| N2—H2B | 0.8900 | C24—C28 | 1.510 (8) |
| N2—H2C | 0.8900 | C25—C26 | 1.369 (10) |
| C9—C11 | 1.351 (7) | C25—H25 | 0.9300 |
| C9—C12 | 1.366 (7) | C26—C27 | 1.383 (10) |
| C10—C13 | 1.368 (8) | C26—H26 | 0.9300 |
| C10—C11 | 1.393 (7) | C27—H27 | 0.9300 |
| C11—H11 | 0.9300 | C28—H28A | 0.9600 |
| C12—C14 | 1.385 (8) | C28—H28B | 0.9600 |
| C12—H12 | 0.9300 | C28—H28C | 0.9600 |
| C13—C14 | 1.376 (9) | Cd1—Cl1 ⁱ | 2.5425 (12) |
| C13—H13 | 0.9300 | Cd1—Cl1 | 2.5425 (12) |
| C14—H14 | 0.9300 | Cd1—Cl2 | 2.6743 (13) |
| C16—C19 | 1.496 (9) | Cd1—Cl2 ⁱ | 2.6743 (13) |
| C16—H16A | 0.9600 | Cd1—Cl3 | 2.6760 (15) |
| C16—H16B | 0.9600 | Cd1—Cl3 ⁱ | 2.6760 (15) |
| C1—N1—H1A | 109.5 | C17—C15—N3 | 118.5 (5) |
| C1—N1—H1B | 109.5 | C15—N3—H3A | 109.5 |
| H1A—N1—H1B | 109.5 | C15—N3—H3B | 109.5 |
| C1—N1—H1C | 109.5 | H3A—N3—H3B | 109.5 |
| H1A—N1—H1C | 109.5 | C15—N3—H3C | 109.5 |
| H1B—N1—H1C | 109.5 | H3A—N3—H3C | 109.5 |

| | | | |
|-------------|-----------|---------------------------|-----------|
| C4—C1—C2 | 121.4 (5) | H3B—N3—H3C | 109.5 |
| C4—C1—N1 | 118.5 (5) | C15—C17—C20 | 118.4 (6) |
| C2—C1—N1 | 120.1 (5) | C15—C17—H17 | 120.8 |
| C1—C2—C3 | 121.0 (5) | C20—C17—H17 | 120.8 |
| C1—C2—H2 | 119.5 | C15—C18—C19 | 120.6 (6) |
| C3—C2—H2 | 119.5 | C15—C18—H18 | 119.7 |
| C2—C3—C6 | 117.1 (6) | C19—C18—H18 | 119.7 |
| C2—C3—C7 | 120.4 (6) | C18—C19—C21 | 117.7 (6) |
| C6—C3—C7 | 122.5 (6) | C18—C19—C16 | 121.0 (6) |
| C1—C4—C5 | 118.8 (6) | C21—C19—C16 | 121.3 (6) |
| C1—C4—H4 | 120.6 | C17—C20—C21 | 119.7 (6) |
| C5—C4—H4 | 120.6 | C17—C20—H20 | 120.1 |
| C4—C5—C6 | 119.7 (6) | C21—C20—H20 | 120.1 |
| C4—C5—H5 | 120.2 | C19—C21—C20 | 121.6 (6) |
| C6—C5—H5 | 120.2 | C19—C21—H21 | 119.2 |
| C5—C6—C3 | 122.0 (6) | C20—C21—H21 | 119.2 |
| C5—C6—H6 | 119.0 | C22—N4—H4A | 109.5 |
| C3—C6—H6 | 119.0 | C22—N4—H4B | 109.5 |
| C3—C7—H7A | 109.5 | H4A—N4—H4B | 109.5 |
| C3—C7—H7B | 109.5 | C22—N4—H4C | 109.5 |
| H7A—C7—H7B | 109.5 | H4A—N4—H4C | 109.5 |
| C3—C7—H7C | 109.5 | H4B—N4—H4C | 109.5 |
| H7A—C7—H7C | 109.5 | C25—C22—C23 | 121.5 (5) |
| H7B—C7—H7C | 109.5 | C25—C22—N4 | 119.1 (5) |
| C10—C8—H8A | 109.5 | C23—C22—N4 | 119.4 (5) |
| C10—C8—H8B | 109.5 | C22—C23—C24 | 120.0 (5) |
| H8A—C8—H8B | 109.5 | C22—C23—H23 | 120.0 |
| C10—C8—H8C | 109.5 | C24—C23—H23 | 120.0 |
| H8A—C8—H8C | 109.5 | C27—C24—C23 | 118.8 (5) |
| H8B—C8—H8C | 109.5 | C27—C24—C28 | 119.7 (6) |
| C9—N2—H2A | 109.5 | C23—C24—C28 | 121.5 (6) |
| C9—N2—H2B | 109.5 | C22—C25—C26 | 118.6 (6) |
| H2A—N2—H2B | 109.5 | C22—C25—H25 | 120.7 |
| C9—N2—H2C | 109.5 | C26—C25—H25 | 120.7 |
| H2A—N2—H2C | 109.5 | C25—C26—C27 | 120.3 (7) |
| H2B—N2—H2C | 109.5 | C25—C26—H26 | 119.8 |
| C11—C9—C12 | 122.6 (5) | C27—C26—H26 | 119.8 |
| C11—C9—N2 | 119.2 (4) | C24—C27—C26 | 120.8 (6) |
| C12—C9—N2 | 118.2 (5) | C24—C27—H27 | 119.6 |
| C13—C10—C11 | 118.0 (5) | C26—C27—H27 | 119.6 |
| C13—C10—C8 | 121.5 (5) | C24—C28—H28A | 109.5 |
| C11—C10—C8 | 120.5 (5) | C24—C28—H28B | 109.5 |
| C9—C11—C10 | 120.1 (5) | H28A—C28—H28B | 109.5 |
| C9—C11—H11 | 119.9 | C24—C28—H28C | 109.5 |
| C10—C11—H11 | 119.9 | H28A—C28—H28C | 109.5 |
| C9—C12—C14 | 117.6 (5) | H28B—C28—H28C | 109.5 |
| C9—C12—H12 | 121.2 | Cl1 ⁱ —Cd1—Cl1 | 180.0 |
| C14—C12—H12 | 121.2 | Cl1 ⁱ —Cd1—Cl2 | 91.13 (5) |

supplementary materials

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|-----------------|------------|--|------------|
| C10—C13—C14 | 121.3 (5) | C11—Cd1—Cl2 | 88.87 (5) |
| C10—C13—H13 | 119.3 | Cl1 ⁱ —Cd1—Cl2 ⁱ | 88.87 (5) |
| C14—C13—H13 | 119.3 | Cl1—Cd1—Cl2 ⁱ | 91.13 (5) |
| C13—C14—C12 | 120.3 (6) | Cl2—Cd1—Cl2 ⁱ | 180.0 |
| C13—C14—H14 | 119.8 | Cl1 ⁱ —Cd1—Cl3 | 89.47 (5) |
| C12—C14—H14 | 119.8 | Cl1—Cd1—Cl3 | 90.53 (5) |
| C19—C16—H16A | 109.5 | Cl2—Cd1—Cl3 | 89.47 (5) |
| C19—C16—H16B | 109.5 | Cl2 ⁱ —Cd1—Cl3 | 90.53 (5) |
| H16A—C16—H16B | 109.5 | Cl1 ⁱ —Cd1—Cl3 ⁱ | 90.53 (5) |
| C19—C16—H16C | 109.5 | Cl1—Cd1—Cl3 ⁱ | 89.47 (5) |
| H16A—C16—H16C | 109.5 | Cl2—Cd1—Cl3 ⁱ | 90.53 (5) |
| H16B—C16—H16C | 109.5 | Cl2 ⁱ —Cd1—Cl3 ⁱ | 89.47 (5) |
| C18—C15—C17 | 122.0 (5) | Cl3—Cd1—Cl3 ⁱ | 180.0 |
| C18—C15—N3 | 119.5 (5) | | |
| C4—C1—C2—C3 | 0.0 (8) | C18—C15—C17—C20 | 0.2 (10) |
| N1—C1—C2—C3 | 177.8 (5) | N3—C15—C17—C20 | 178.3 (6) |
| C1—C2—C3—C6 | 0.0 (8) | C17—C15—C18—C19 | 0.0 (9) |
| C1—C2—C3—C7 | −177.9 (6) | N3—C15—C18—C19 | −178.1 (5) |
| C2—C1—C4—C5 | −1.1 (9) | C15—C18—C19—C21 | −0.5 (9) |
| N1—C1—C4—C5 | −178.8 (5) | C15—C18—C19—C16 | 178.6 (6) |
| C1—C4—C5—C6 | 2.1 (9) | C15—C17—C20—C21 | 0.0 (11) |
| C4—C5—C6—C3 | −2.1 (10) | C18—C19—C21—C20 | 0.7 (10) |
| C2—C3—C6—C5 | 1.1 (9) | C16—C19—C21—C20 | −178.3 (7) |
| C7—C3—C6—C5 | 178.9 (6) | C17—C20—C21—C19 | −0.5 (12) |
| C12—C9—C11—C10 | −0.6 (8) | C25—C22—C23—C24 | −0.3 (9) |
| N2—C9—C11—C10 | 178.3 (5) | N4—C22—C23—C24 | 178.0 (5) |
| C13—C10—C11—C9 | 0.2 (8) | C22—C23—C24—C27 | 1.2 (9) |
| C8—C10—C11—C9 | −179.4 (5) | C22—C23—C24—C28 | −178.8 (6) |
| C11—C9—C12—C14 | 0.8 (8) | C23—C22—C25—C26 | −0.2 (12) |
| N2—C9—C12—C14 | −178.2 (5) | N4—C22—C25—C26 | −178.5 (7) |
| C11—C10—C13—C14 | 0.0 (9) | C22—C25—C26—C27 | −0.3 (14) |
| C8—C10—C13—C14 | 179.7 (6) | C23—C24—C27—C26 | −1.7 (12) |
| C10—C13—C14—C12 | 0.2 (10) | C28—C24—C27—C26 | 178.4 (8) |
| C9—C12—C14—C13 | −0.6 (9) | C25—C26—C27—C24 | 1.2 (15) |

Symmetry codes: (i) $-x+1, -y, -z$.

Hydrogen-bond geometry (Å, °)

| $D—H\cdots A$ | $D—H$ | $H\cdots A$ | $D\cdots A$ | $D—H\cdots A$ |
|---|-------|-------------|-------------|---------------|
| N1—H1A ⁱⁱ —Cl5 ⁱⁱ | 0.89 | 2.38 | 3.264 (5) | 176 |
| N1—H1B ⁱⁱⁱ —Cl4 ⁱⁱⁱ | 0.89 | 2.47 | 3.309 (5) | 157 |
| N1—H1C ^{iv} —Cl2 ^{iv} | 0.89 | 2.54 | 3.329 (5) | 148 |
| N1—H1C ^v —Cl3 ^v | 0.89 | 2.88 | 3.427 (5) | 121 |
| N2—H2A ^{vi} —Cl4 ^{vi} | 0.89 | 2.38 | 3.265 (5) | 176 |
| N2—H2B ^{vii} —Cl3 ^{vii} | 0.89 | 2.51 | 3.300 (5) | 149 |

| | | | | |
|------------------------------|------|------|-----------|-----|
| N2—H2B···Cl2 ^{vii} | 0.89 | 2.93 | 3.495 (5) | 123 |
| N2—H2C···Cl5 ^{viii} | 0.89 | 2.33 | 3.186 (5) | 162 |
| N3—H3A···Cl4 | 0.89 | 2.37 | 3.254 (5) | 172 |
| N3—H3B···Cl3 ^{viii} | 0.89 | 2.61 | 3.344 (5) | 140 |
| N3—H3B···Cl2 ^{viii} | 0.89 | 2.75 | 3.367 (5) | 127 |
| N3—H3C···Cl5 ^{vii} | 0.89 | 2.44 | 3.289 (5) | 159 |
| N4—H4A···Cl4 | 0.89 | 2.40 | 3.270 (5) | 167 |
| N4—H4B···Cl5 ^{vii} | 0.89 | 2.38 | 3.267 (5) | 177 |
| N4—H4C···Cl2 | 0.89 | 2.55 | 3.305 (5) | 143 |
| N4—H4C···Cl3 | 0.89 | 2.91 | 3.526 (5) | 128 |

Symmetry codes: (ii) $-x+1, -y+1, -z+1$; (iii) $-x+2, -y, -z+1$; (iv) $x, y, z+1$; (v) $-x+1, -y, -z+1$; (vi) $x, y+1, z$; (vii) $-x+1, -y+1, -z$; (viii) $x+1, y, z$.

supplementary materials

Fig. 1

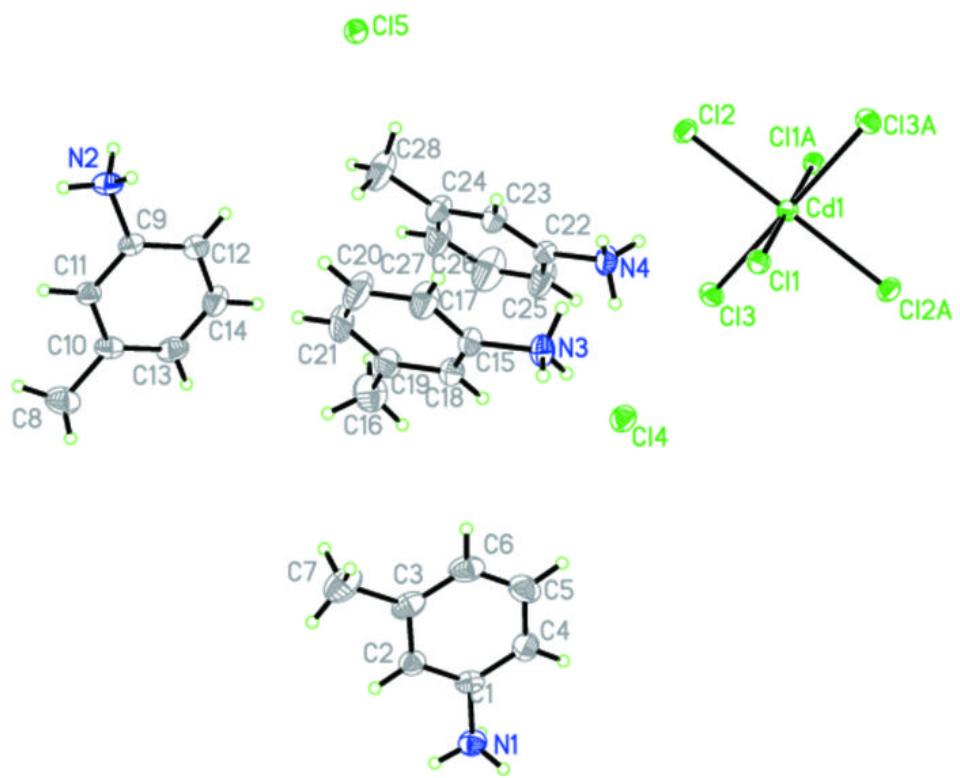


Fig. 2

